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THERMAL ANALYSIS OF PMR-POLYIMIDES BY DIELECTROMETRY

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ABSTRACT

A preliminary study was conducted to determine the dielectric properties of glass fabric reinforced composites as influenced by the reactions occurring during the preparation of crosslinked polyimides by the PMR process. The variables studied included: formulated molecular weight, staging temperature and time; rate of temperature increase to cure temperature; and cure temperature and time. The changes of capacitance and, particularly, of dissipation factor were found to be strongly dependent on each of the variables studied.

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SUMMARY

The dielectric properties (especially the dissipation factor) of glass fabric reinforced composites as influenced by the reactions occurring during thermal processing of monomer reactants (PMR) to high temperature resistant polyimides are described in this report. The effects of the following variables are presented and discussed: 1) the heating and re-heating (after air drying) of glass cloth impregnated with a methanol solution of the three monomers BTDE, MDA, and NE (see table I); 2) staging temperature and time; 3) resin composition (i. e., relative amounts of the three monomers); and 4) heating rate, maximum cure temperature, pressing pressure, and measurement frequency. It was found that all of these variables caused changes in the electrical property behavior. Based on this it is concluded that measurement of dielectric properties under controlled test conditions is a promising method for characterization of this class of materials during reaction.

INTRODUCTION

A class of highly processable, high temperature resistant polyimides has been developed at the NASA Lewis Research Center. These unique addition-type polyimides can be used as matrix resins in fiber reinforced composites, as adhesives, and as molding powders. The advantages of these polyimides over commercially available condensation-type polyimides include: 1) processing versatility, 2) improved high temperature performance, 3) greater safety to fabricators, and 4) lower costs.

The process for fabricating fiber-reinforced composites using this class of polyimides as the matrix material consists of applying monomeric reactants in solution to the fiber (e. g., glass or graphite) and of

effecting polymerization in situ by a combination of heat and pressure. For convenience this has been called the PMR process (polymerization of monomer reactants) and is reviewed in ref. 1. A number of variables can be manipulated in this process including: 1) the temperature-time-pressure program, 2) the composition of the monomer-solvent mixture, 3) the specimen geometry, and 4) fiber type and amount.

A variety of techniques are being employed to identify the critical processing variables, to identify the critical processing variables, to obtain an improved understanding of the physical and chemical changes occurring during the process, to aid in selection of the proper combination of conditions for "tailor-making" composites with desired properties, to aid in quality control, and to develop practical methods for monitoring the state of composites during processing.

The purpose of this report is to describe a preliminary study of the influence of the reactions occurring during the preparation of crosslinked polyimides by the PMR process on the dielectric properties (particularly the dissipation factor) of glass fabric reinforced composites. For convenience, glass fabric was used instead of graphite fiber for this study of resin behavior primarily because the electrical conductivity of graphite necessitates a somewhat more complicated test specimen-electrode configuration. The variables investigated include: 1) the formulated molecular weight (i.e., the ratio of monomers (see ref. 1), 2) "staging" time and temperature (staging refers to a low temperature heat treatment preliminary to forming under pressure at higher temperatures), 3) the time-temperature program for the "curing" process (i.e., heating rate and maximum temperature effects), 4) applied pressure, 5) temperature recycle, and 6) measurement frequency.

Although dielectrometry has been applied to polyimides by others (see for example, refs. 2 and 3), a systematic screening of the effects of all of these variables has not been done.

EXPERIMENTAL

Materials

The materials used in this study included the monomers for preparing PMR polyimides: 1) monomethyl ester of 5-norbornene - 2, 3-dicarboxylic acid (NE), 2) 4, 4'-methylenedianiline (MDA), and 3) the dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (BTDE) (see table I). These were obtained from commercial sources except for the BTDE which was prepared from the anhydride (BTDA) by refluxing with enough methanol to form a 50 weight percent solution of BTDE in methanol. Other materials used were: 1) anhydrous methanol as solvent to prepare 50 weight percent solutions of the monomers, 2) heat cleaned glass fabric for preparation of composites, 3) Kapton film as an electrical insulating material, and 4) aluminum foil for electrodes. Also a commercial polysulfone (see table I) was included as an example of a high temperature thermoplastic polymer. Methylene chloride (CH_2Cl_2) was used as the solvent for the polysulfone.

Preparation of Composite Specimens

Solutions containing 50 percent by weight solids in anhydrous methanol were prepared using the monomers NE, MDA, and BTDE in the desired combinations and ratios. Solutions of the three monomers were prepared with formulated molecular weights (FMW) of 1000, 1250, 1500, 1750, and 2000 (corresponding to PMR 10, PMR 12.5, PMR 15, etc.) The expression used for FMW is:

$$\text{FMW} = n \text{ MW}_{\text{BTDE}} + (n + 1) \text{ MW}_{\text{MDA}} + 2 \text{ MW}_{\text{NE}} - 2(n + 1) \left(\text{MW}_{\text{H}_2\text{O}} + \text{MW}_{\text{CH}_3\text{OH}} \right)$$

where MW_{BTDE} , MW_{MDA} etc., are the molecular weights of the materials indicated in the subscripts (see ref. 1). Thus the molar ratios of NE:MDA:BTDE equal $2:(n + 1):n$. Also, solutions having molar ratios

of 2:1 for NE:MDA and 1:1 for BTDE:MDA were prepared as well as a solution of MDA by itself. The composites were prepared by impregnating glass fabric with the solutions and allowing to dry in air for several days. The weight of solid monomer was about 0.023 grams per square centimeter of fabric (0.15 grams per square in.). This material is subsequently referred to as "unstaged". In the case of the polysulfone, 10 grams were dissolved in 80 mls. of CH_2Cl_2 , applied to glass cloth, and air dried. The dried composite material was cut into approximately 3 cm squares. "Staged" PMR composites were prepared by heating "unstaged" composite material in a hot air oven to remove residual solvent and to imidize (see ref. 4). Most of the specimens were staged for one hour at 204°C . The thickness of specimens staged at 204°C for one hour was 0.052 ± 0.005 cm (0.020 ± 0.002 in.). Some specimens were staged for times ranging from 5 minutes to 3 hours and at temperatures ranging from 121° to 232°C to study the effects of staging conditions on electrical properties during subsequent heat treatment.

APPARATUS AND PROCEDURE

The apparatus used in this work is shown schematically in fig. 1 and includes: 1) a commercial dielectrometer (ref. 5) that will continuously measure both the capacitance (from 0 to 500 pf) and the dissipation factor (from 0 to 1) at a frequency in the range from 0.1 to 1.0 kHz, 2) an 'XYY' recorder, 3) a shielded test cell for dielectric specimens, 4) a press with 11.4 cm (4 1/2 in.) square heated platens capable of operation up to a temperature of about 350°C and a pressure of about $8.3 \times 10^6 \text{ N/m}^2$ (1200 PSIG), and 5) a temperature controller with capability of generating linear ramps ranging from 1° to 9°C per minute. (Note: The dissipation factor, DF or $\tan \delta$, is defined as the ratio of loss current to charging current. This assumes that the dielectric material corresponds in its electrical behavior to a capacitor with a resistor in parallel- i.e., an RC circuit). Primary emphasis was given to measurement of changes in dissipation factor

because there was expected to be relatively little effect of sample thickness or area on the dissipation factor compared to the effect on capacitance.

The dielectric specimen usually consisted of three 2.54 cm (1 in.) square pieces of the impregnated glass fabric stacked to form a laminate. This laminate was contacted, in the case of staged material, by using 2.54 cm (1 in.) square pieces of aluminum foil as plates to form a capacitor. In cases where unstaged material was studied, an additional layer of 0.0025 cm (0.001 in.) thick Mylar was placed on each plate in series with the capacitor. This was done because otherwise the maximum dissipation factor for unstaged material often exceeded the range of the dielectrometer.

The temperature of one of the platens of the press was sensed by a thermocouple which served as input to the temperature controller and to a digital temperature readout. The temperature of the specimen lagged that of the controller. Temperature correction factors for each of the heating rates used were determined experimentally using a thermocouple in the specimen. This was done to avoid the inconvenience of placing a thermocouple inside the specimen cell for every run. Usually a temperature gradient of 9°C per minute was employed to a maximum temperature of 317°C , but rates of 3°C per minute and 24.5°C per minute (not linear) and maximum temperatures of 290°C and 345°C also were tested for qualitative comparison. During a run, the pen carriage of the recorder was swept along the x-axis at a constant rate of 0.025 cm (0.01 in.) per second and the DF and C outputs of the dielectrometer were recorded as Y and Y' by the two recorder pens (usually both at a sensitivity of 0.04 volt per cm (0.1 volt per in.) corresponding to a capacity change of 19.7 pf per cm (50 pf per in.) and a DF change of 0.04 per cm (0.1 per in.)). Pressure was applied to the specimen at the beginning of a run and, for the purposes of this study, was not varied during any single run. This pressure usually was $1.7 \times 10^5 \text{ N/m}^2$ (25 PSIG) but pressures of $6.9 \times 10^5 \text{ N/m}^2$ (100 PSIG) and $2.8 \times 10^6 \text{ N/m}^2$ (400 PSIG) also were used. The thickness of a three-ply

specimen after a typical run (PMR 15 staged at 204°C for 1 hour and then heated at $9^{\circ}\text{C}/\text{min}$ to 317°C at $1.7 \times 10^5 \text{ N/m}^2$) was 0.064 cm (0.025 in.).

RESULTS

The next several sections present the experimental results on the effects of several variables on the dissipation factor and, in some cases, the capacitance of the materials under study. Generally, only relative changes in the values of DF and of C are shown on the figures in this report. Also in several instances, for ease of comparison, several curves are plotted in the same figure by displacing them in the direction of the y-axis. Sections on the following topics are included: 1) effect of heating and reheating of unstaged PMR-15; 2) effect of staging temperature and time on PMR-15; 3) effect of resin composition; and 4) effects of heating rate, maximum temperature, pressing pressure, and frequency.

Heat and Reheat of Unstaged PMR-15

The solid curves on fig. 2 show the changes of dissipation factor (DF) and of capacitance (C) for unstaged PMR-15 on glass cloth as the temperature was increased at the rate of $9^{\circ}\text{C}/\text{min}$ to 317°C and then held at 317°C for times up to about 15 minutes. (The initial unchanging parts of the curve in the temperature range of 22°C to 60°C are not shown). The dashed curves show the variation of DF and C during a repeat of the thermal cycle of the same specimen after cooling to room temperature, 22°C . During the initial heating of the specimen, three major peaks occurred in the dissipation factor at 93°C , 157°C , and 303°C and one major peak occurred in the capacitance between 93°C and 157°C with a maximum at about 140°C . A smaller peak in the capacitance curve is observed at about 290°C . Upon cooling to room temperature and reheating, none of the peaks appear. There are, however, small permanent changes in C and DF.

The data just presented show the results of heating and reheating of unstaged PMR-15 to 317°C at a rate of $9^{\circ}\text{C}/\text{min}$. It was of interest to see if heating a specimen through the first peak in the DF (at 93°C) caused some permanent change in the resin. Figure 3 shows the effect on DF and C of heating unstaged PMR-15 to 115°C at the rate of $9^{\circ}\text{C}/\text{min}$, quickly cooling to room temperature, and then reheating to 115°C at $9^{\circ}\text{C}/\text{min}$. Apparently no permanent change as detected by the DF or C resulted from this treatment. Figure 4 shows the response of DF and C to the melting of MDA. A sharp increase in DF and C is followed by a gradual increase as the viscosity of the melt decreases with increase in temperature. (This determination of the melting point of MDA also served as a check on the temperature correction used in these experiments.) Heating of unstaged PMR-15 at $9^{\circ}\text{C}/\text{min}$ to 195°C and thus through the second peak in the DF at 157°C (see fig. 5) resulted in a permanent change in the electrical behavior of the material as shown by the change in the DF and C curves on reheating the specimen.

For a comparison to the behavior of PMR-15, fig. 6 shows the variation of C and DF for a thermoplastic resin, polysulfone P-1700, during three thermal cycles of the same specimen at a heating rate of $9^{\circ}\text{C}/\text{min}$ to 250°C . All three runs show essentially the same DF and C response and thus no permanent change in the resin. A small difference in the leading edge of the 202°C peak on the first heating is believed to be due to the specimen/electrode interface. This type of leading edge is also noted on the first heat of the polyimide specimens.

Effect of Staging Temperature and Time on PMR-15

As pointed out in the experimental section of this report, two of the steps in the fabrication of fiber-reinforced polyimide matrix composites by the PMR process consist of solvent removal by air drying at room temperature or at slightly elevated temperature ($\sim 60^{\circ}\text{C}$) followed by heating in a hot-air oven to effect imidization and removal of condensation products. This latter process is called "staging" and typically is performed at a temperature in the range of 121° to 204°C and

for a time in the range of 1 to 3 hours. In this section the effects of the two principal staging variables, temperature and time, on the subsequent changes in DF of the FMR-15 during heating to 317°C at $9^{\circ}\text{C}/\text{min}$ are presented.

Figure 7 shows the effect on variation of DF of five staging temperatures ranging from 121°C to 232°C for a constant staging time of one hour. As the staging temperature increases the temperature at which the first increase in DF occurs becomes greater (ranging from 160°C to 225°C), and for the three lowest staging temperatures an additional peak appears in the 222°C to 229°C range. Finally, the peak occurring in the 298°C to 302°C range has its maximum at essentially the same temperature for all five staging temperatures but the relative height of the maximum for the 232°C staged material is about one-half that of the others.

The effect of change in staging time from 5 to 180 minutes for a constant staging temperature of 204°C on variations of DF is shown in fig. 8. The temperature of initial increase in DF shows only a minor change with staging time (204°C to 213°C). The curves for the 5 and 15 minute staging times show second peaks at 233°C and 255°C , respectively. The third or high temperature peak occurs at essentially the same temperature for all staging conditions (i. e., at 296°C to 299°C). Also this peak has about the same relative height in all cases.

The final figure for this section (fig. 9) shows the changes in DF and C for PMR-15 (staged at 204°C for 1 hour) as the temperature is increased from room temperature to 317°C at $9^{\circ}\text{C}/\text{min}$, held at 317°C for about 15 minutes, cooled, and recycled. The sensitivity on the capacitance scale is 10 times that indicated on previous figures. As previously noted for unstaged material a permanent change in DF and C occurs as a result of the first heat treatment. And the DF and C each appear to approach a constant value asymptotically with time at 317°C .

Effects of Resin Composition

The variation of dissipation factor with temperature during $9^{\circ}\text{C}/\text{min}$ heating to 317°C is shown in fig. 10 for staged specimens of PMR-

polyimide of formulated molecular weights (FMW) 1000, 1250, 1500, 1750, and 2000. The temperature at the first break in the DF curve increases from 188° to 227° C as the FMW increases from 1000 to 2000. The temperature at the maximum DF appears to increase slightly with molecular weight. The height of the DF maximum decreases with increasing molecular weight in the ratio of 3.1:2.1.8:1.2:1.

A comparison of the DF curves for staged PMR-15, 2NE/MDA; and BTDE/MDA is shown in fig. 11. The most important detail to notice is that the curve for BTDE/MDA shows no discernable maximum.

Effects of Heating Rate, Maximum Temperature, Pressure, and Frequency

The effect of variation of heating rate, maximum temperature, pressure, and frequency were briefly examined and are discussed below. The effects of different heating rate on the dissipation factor of staged PMR-15 are summarized in fig. 12. (Note that the curve for the 3° C/min heating rate is plotted in three segments.) The major differences caused by change in heating rate are in the high temperature maximum. The maximum occurs at different temperatures and, in the case of the 3° C/min heating rate, the maximum is much lower in height.

The effects of maximum cure temperatures of 290° , 317° , and 345° C are shown in fig. 13. As expected there is no change in the temperature of first increase in DF. But the maximum of the high temperature peak undergoes a shift from 281° to 326° C as the maximum cure temperature is increased from 290° to 345° C. Also the height of the peak increases with temperature in the relative ratios of 1:1.8:2 as the temperature increases from 290° to 345° C.

The only result of increasing pressing pressure from 1.7×10^5 N/m² (25 psig) to 2.6×10^6 N/m² (400 psig) was to lower the temperature at which the first increase in dissipation factor occurred (see fig. 14).

The effect of a frequency change from 1000 Hz to 100 Hz on the DF of staged PMR-15 is shown in fig. 15. The dissipation factor at the maximum increased from about 0.2 to 1 for the specimen and conditions selected.

DISCUSSION OF RESULTS

A simplified outline of the chemistry of the PMR-polyimide reaction sequence as it is understood at present is shown in fig. 16. First, condensation reactions occur between the amine and the ester and carboxyl groups to form imide rings and the volatiles, water and methanol. The average chain length of the molecules formed is determined primarily by the relative amount of nadic ester (NE) present. At higher temperatures addition-type reactions occur at the nadic end groups by a complex set of reactions involving chain extension and an unknown degree of cross linking (ref. 7).

The changes in DF and C of unstaged PMR-15 material when heated at 9°C per minute to 317°C , held at 317°C for a time, and cooled to room temperature and reheated according to the same program are shown in fig. 2. A detailed understanding of the dielectric changes would require extensive chemical analysis of specimens withdrawn at various points during the heating cycle and correlation of the dielectrometry results with those obtained by other techniques such as DTA and viscosity measurements. Although this was not attempted because the main purpose of this report is to show the effects of processing variables on the changes in dielectric properties, several observations can be made on the nature of the peaks for PMR-15 in fig. 2. These are as follows:

- 1) Comparing the behavior of PMR-15 to that of a thermoplastic, polysulfone, shown in fig. 6, indicates that a permanent chemical change has occurred in PMR-15 after the first cycle and essentially no change in the polysulfone.
- 2) Heating PMR-15 through the first major peak in the DF curve (at 93°C) at $9^{\circ}\text{C}/\text{min}$ to 115°C , cooling, and heating to 115°C again (see fig. 3) shows essentially no change in behavior and thus, no chemical reaction appears to have taken place - for example, to form amide-acid. Also, comparison of this PMR-15 peak to the changes occurring in the DF of MDA on melting (fig. 4) shows that the peak apparently is not due to melting alone.
- 3) Raising the temperature of PMR-15 to 195°C through the second peak in the DF curve at 157°C causes permanent change as evidenced by the absence of both the 93°C and 157°C

peaks upon recycle (fig. 5). This second peak corresponds to imidization as demonstrated by infrared spectroscopic studies (see ref. 6). The implication is strong that both steps of the condensation reaction occur practically simultaneously in this 157°C region. This is the so-called "staging" region. 4) The broad peak in the dissipation factor peaking at about 303°C (fig. 2) corresponds to the temperature region where cross-linking is thought to occur (ref. 7). On recycle, this peak no longer appears so it does represent some permanent chemical change in the resin. Some of the factors which affect this peak will be touched on later in this discussion. At a constant temperature of 317°C , after this peak is passed, the DF and C curves appear to slowly approach a constant value.

As previously mentioned, the staging of PMR resin is carried out to bring about imidization. This is intended to eliminate as much as possible of the volatile H_2O and CH_3OH to prevent void formation in the composites at later stages in the process. On the other hand, if staging temperatures and/or times are too great, cross-linking or unwanted side reactions might occur resulting in too little flow and formability upon pressure application and an undesirable end product. Figure 7 shows the effect of varying staging temperature for a fixed staging time on the behavior of the DF upon heating the staged material at the rate of $9^{\circ}\text{C}/\text{min}$ from RT to 317°C (only the portions of the curves above 150°C are shown). The $204^{\circ}\text{C}/1$ hour curve represents the reference conditions. The peaks at 225° , 222° , and 229°C on the 121° , 149° , and 177°C staging temperature curves, respectively, possibly indicate incomplete imidization of the material. The peak in the 300°C region (believed to be related to the cross-linking reaction) is substantially decreased by the $232^{\circ}\text{C}/1$ hour staging conditions and suggests that staging at temperatures this high should be avoided or the staging time reduced. The temperatures at which the first increase in DF occurs differ significantly and increase with staging temperature. This potentially could be used as a criterion for quality control. Since it also indicates the temperature of the first decrease in viscosity it might be of interest in selecting processing conditions.

The effect of staging time at a constant temperature of 204°C on DF is shown in fig. 8. An additional peak is apparent at 233°C for the 5 min-

ute staging time and at 255⁰ C for the 15 minute staging time. This again may indicate incompleteness of imidization under these conditions. Compared to staging temperature, staging time appears to have only a small effect on the temperature of the initial increase in DF.

The behavior of the reference material, PMR-15, staged at the reference conditions of 204⁰ C for 1 hour is plotted on fig. 9. In future studies it would be of interest to analyze the behavior of the C and DF curves after the 298⁰ C peak to obtain information on post-curing effects.

On figs. 10 and 11 the effects of chemical composition of PMR-polyimides on dissipation factor of cured specimens during a 9⁰ C/min heat to 317⁰ C are summarized. Figure 10 shows the effect of formulated molecular weight (FMW) ranging from 1000 to 2000. The temperature of the first break in DF increases significantly with increasing FMW and the height of the maximum in the "cross-linking region" decreases with increasing FMW. But the temperature at which the maximum of this peak occurs does not vary significantly with FMW. The shape of this peak probably is determined by several complex factors including viscosity changes with temperature and rates and mechanisms of chain extension and cross-linking. Figure 11 shows similar information for 2NE/MDA and BTDE/MDA compared to PMR-15. The 2NE/MDA represents a special member of the FMW series (without BTDE) with the smallest FMW (i. e., 490) and with the greatest number of potential cross-links per unit volume. The first break in the DF curve of the 2NE/MDA does not fall in line with those of the 1000-2000 FMW series. The reason for this has not been determined. But the position of the high temperature peak is about the same and this peak follows the trend of increasing height with decreasing FMW. The BTDE/MDA has no end-group cross-linking capability and should form linear polymer chains. There is no maximum in the 300⁰ C range for this material.

In practice, the change in behavior of the DF curve with FMW might be useful in quality control. And the shape of the peak in the 300⁰ C temperature region might aid in the selection of processing conditions for forming polyimide materials. It is of special interest that the high temperature peak always appears very close to 300⁰ C independent of

FMW for the constant test conditions selected and is probably characteristic where NE is used as the end cap. Therefore this technique might be useful in evaluating other cross-linking systems with potential for lower curing temperatures. However, the potential applications of this method were not investigated in the present study.

The effect of the test conditions: 1) temperature gradient, 2) maximum cure temperature, 3) pressure, and 4) frequency were briefly examined and the results are shown on figs. 12, 13, 14, and 15, respectively. One obvious point is that if the electrical behavior during polymerization is to be compared it must be compared under the same controlled conditions.

Of the temperature gradients used (see fig. 12) $3^{\circ}\text{C}/\text{min}$ was unnecessarily time consuming. Otherwise comparisons could probably be made at any constant gradient. The difference in positions of the DF maxima is probably due to the complicated kinetics of the reaction.

Increasing the final cure temperature causes a shift of the maximum in the DF to higher temperatures (fig. 13). This is probably because of a prolonged decrease in viscosity due to the higher temperature. Further work has to be done to see if electrical property measurements are useful to obtain a measure of the relative degree of cure at the different maximum temperatures. Perhaps comparison of recycle curves of these specimens to 345°C would be informative. Or dielectric relaxation measurements of the materials prepared at the different cure temperatures might give useful comparative information.

The range of pressures used did not noticeably affect the temperature or height of the DF maximum (fig. 14) so if there are differences in the reaction in this region due to pressure, this method showed no evidence for them. The effect of pressure on the temperature of the initial change in DF is surprising - unless the material undergoes a volume decrease in softening, or if some species which decreases the softening temperature was retained more effectively at higher pressures.

Finally, a test of the effect of measurement frequency is shown in fig. 15. This shows the expected sensitivity of the measurements to frequency. It is interesting that the sensitivity at the maximum is

greater at 0.1 kHz but on the plateau of the curve just after the initial increase in DF the reverse is true. No explanation is offered for this.

It probably should be emphasized that the effects of the conditions as presented in this report must be clearly recognized before applying dielectric measurements to reacting systems - for example, for monitoring curing of polyimide composites in a press or autoclave.

CONCLUSIONS

A preliminary study of the influence of the reactions occurring during the PMR process on the dielectric properties of glass fiber reinforced composites as a function of materials composition, processing, and test condition variables leads to the following major conclusions:

1. Dielectrometry appears to be particularly useful for following addition polymerization reactions. For example, it is a good method for monitoring reactions occurring during the PMR process for fabrication of fiber reinforced polyimides and could be used for quality control and for monitoring the effects of processing conditions.

2. Repeated heating of air dried unstaged monomer mixtures to about 115⁰ C causes no change and, therefore, the unstaged material appears to have sufficient chemical stability to be stored at ambient temperatures.

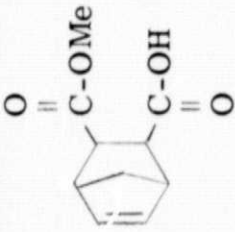
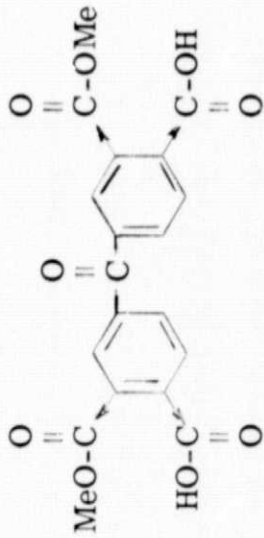
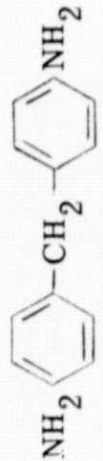
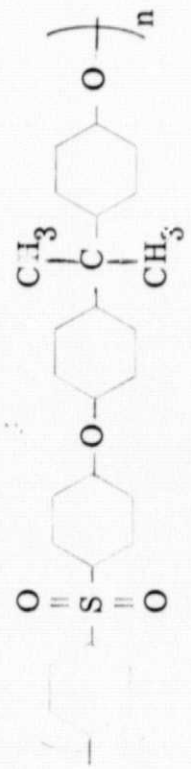
3. The staging conditions of one hour at 204⁰ C appear to be a good compromise between incomplete imidization and undesirable premature crosslinking or decomposition resulting in potentially inferior processability.

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TABLE I. - STRUCTURES OF PMR MONOMERS AND OF A POLYSULFONE

Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethyl ester of 3,3',4,4'- benzophenonetetracarboxylic acid	BTDE
	4,4'-methylenedianiline	MDA
	Poly(ether-sulfone) from bisphenol-A and bischlorophenyl sulfone	PES

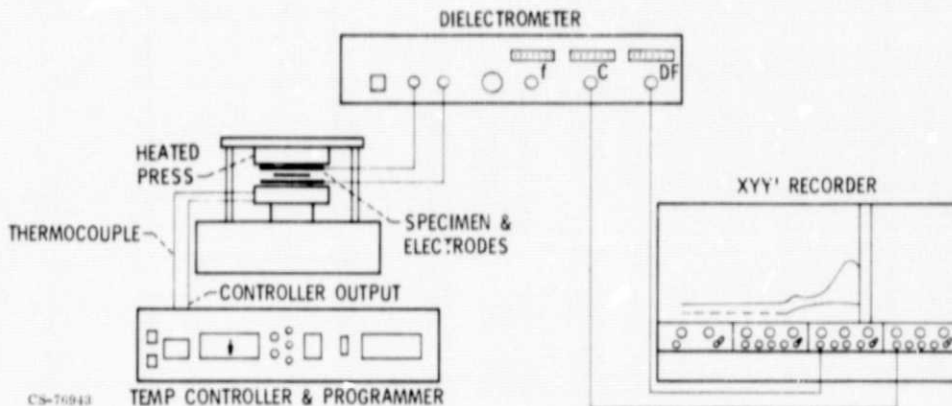


Figure 1. - Dielectric measurements apparatus.

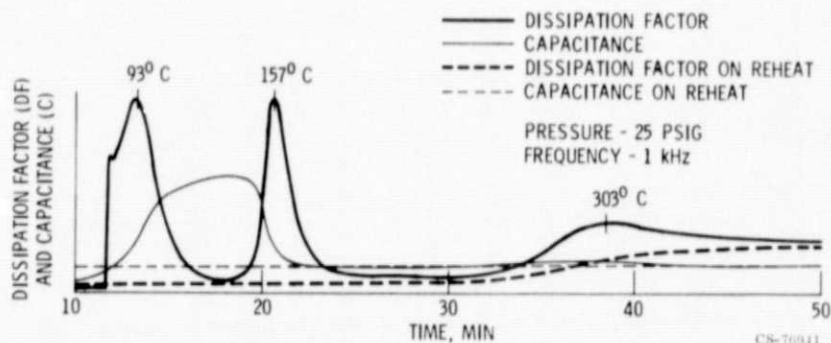


Figure 2. - Variation of dissipation factor and capacitance of unstaged PMR-15 on glass cloth during heating and reheating to 317°C at 9°C/min (3 ply - 1 in.², 2 mils Kapton).

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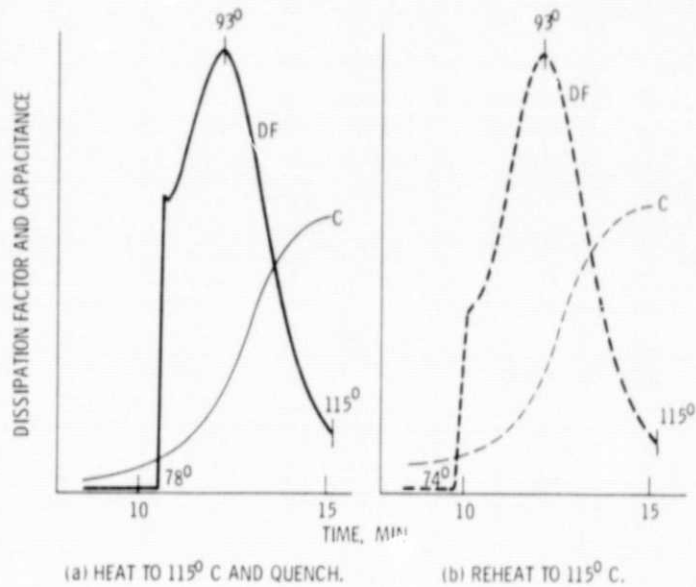


Figure 3. - Effect of thermal cycle on 93°C peak of DF of PMR 15 heated to 115°C at 9°C/min ($f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in.², 2 mils Kapton).

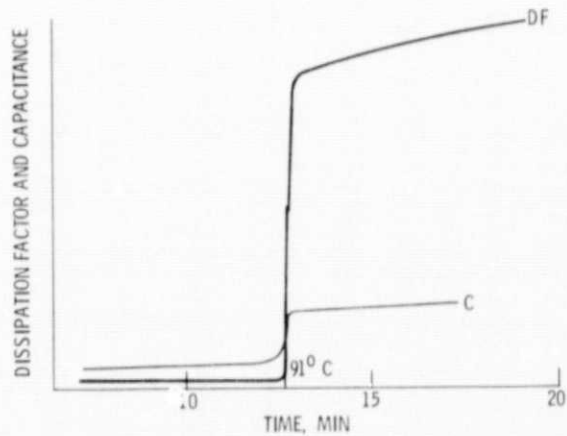


Figure 4. - The change of DF and C on melting of MDA at a heating rate of 9°C/min ($f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in.²).

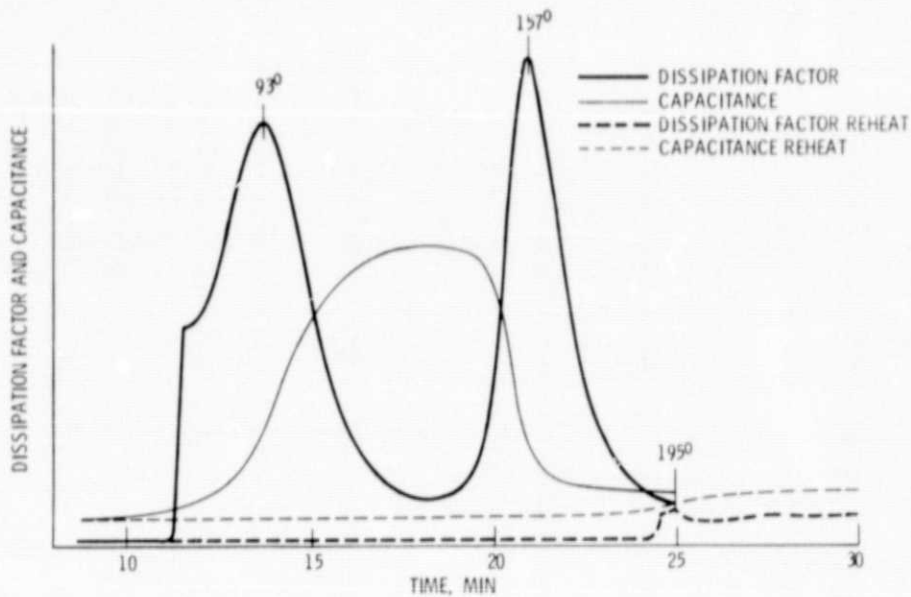


Figure 5. - Effect of thermal cycle on 93° C and 157° C peaks of DF of PMR 15 heated to 195° C at 9° C/min ($f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in. 2 , 2 mils Kapton).

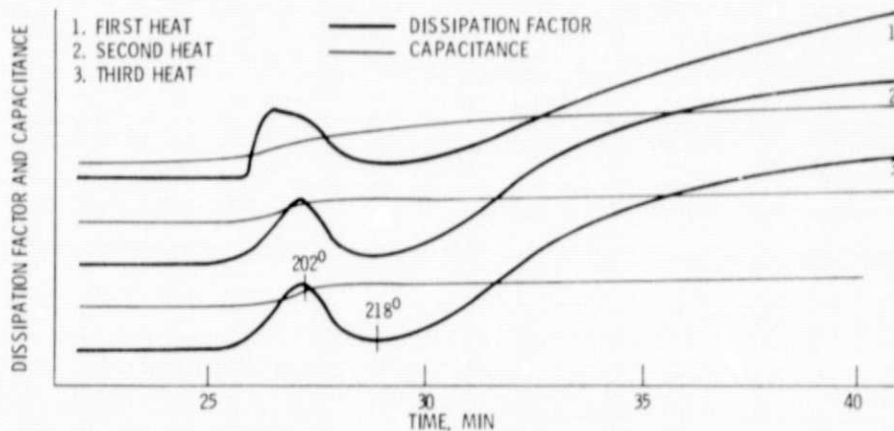


Figure 6. - Effect of 9° C/min grad. to 250° C and reheating on DF of P-1700 polysulfone, a high temperature thermoplastic ($f = 1$ kHz, 50 psig, 3 ply - 1 in. 2).

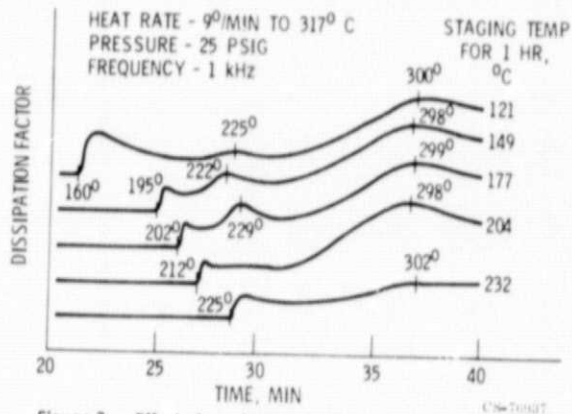


Figure 7. - Effect of staging temperature on the change of DF with temperature and time of PMR-15.

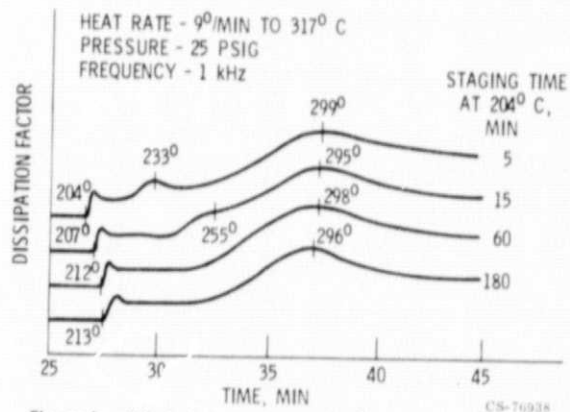


Figure 8. - Effect of staging time at 204°C on change in DF with temperature and time for PMR-15.

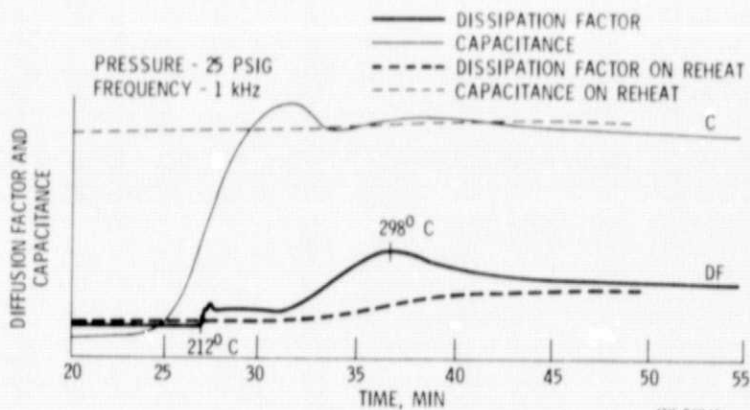


Figure 9. - Variation of DF and C of PMR-15 staged at 204⁰ C for one hour during heating and reheating to 317⁰ C at 9⁰ C/min.

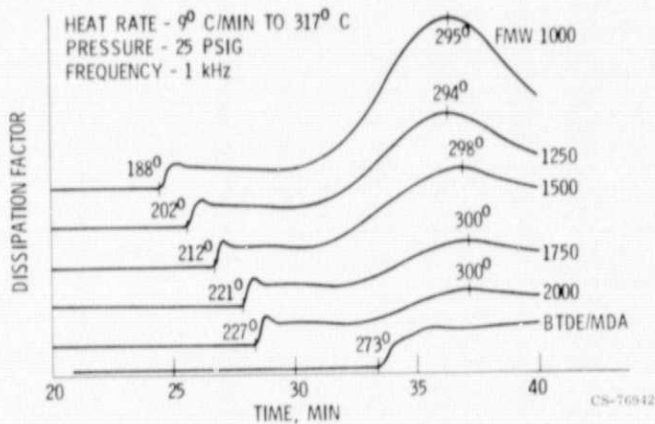


Figure 10. - Effect of formulated molecular weight on the change of DF with temperature and time of PMR-PI staged at 204⁰ C for one hour.

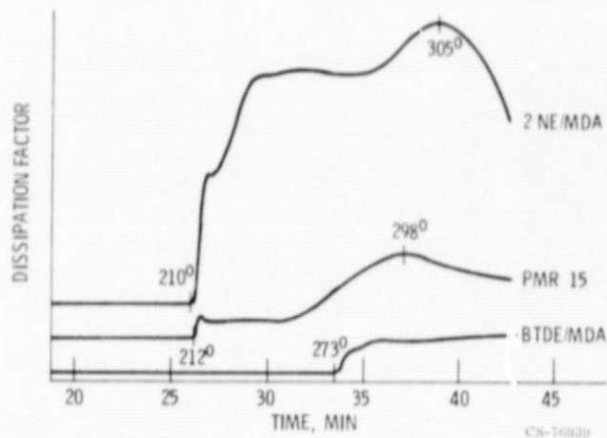


Figure 11. - Comparison of DF changes with temperature and time for three monomer mixtures (staged 205°C/1 hr, HTG rate 9°C/min to 317°C, $f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in.²).

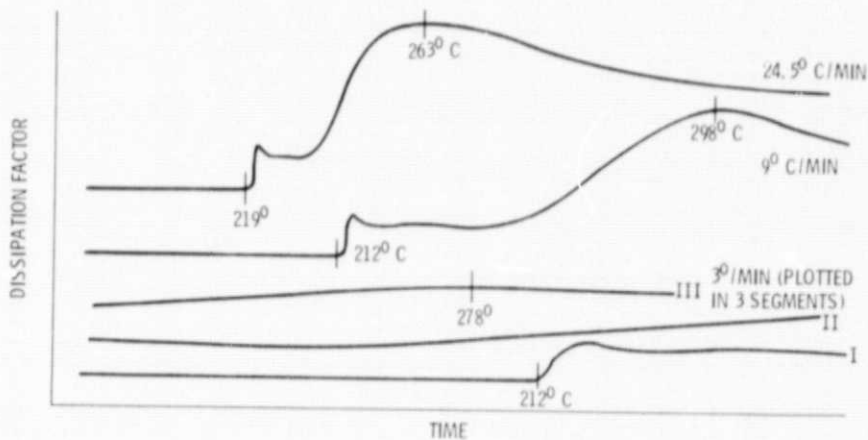


Figure 12. - Effect of heating rate on DF change with temperature and time for PMR 15 staged at 204°C for one hour (max. temp. 317°C, $f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in.²).

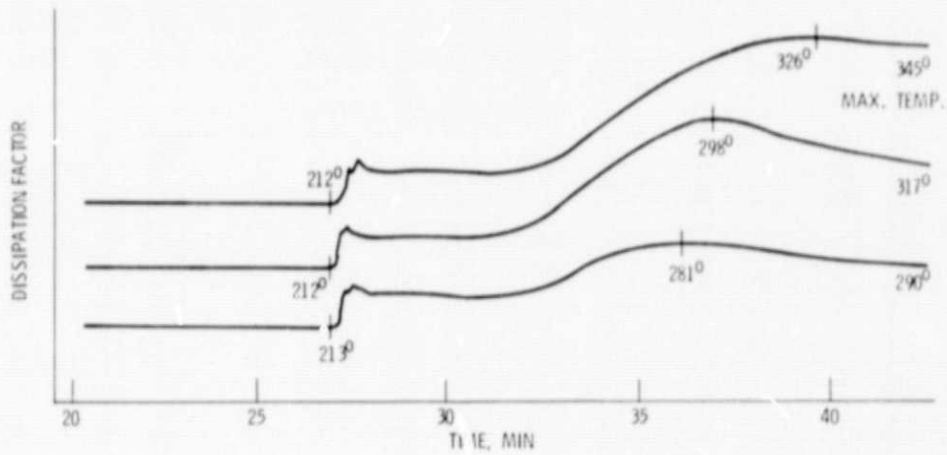


Figure 13. - Effect of maximum cure temperature on DF change with temperature and time for PMR 15 staged at 204° C for one hour (heat rate 9° C/min, $f = 1$ kHz, $P = 25$ psig, 3 ply - 1 in.).

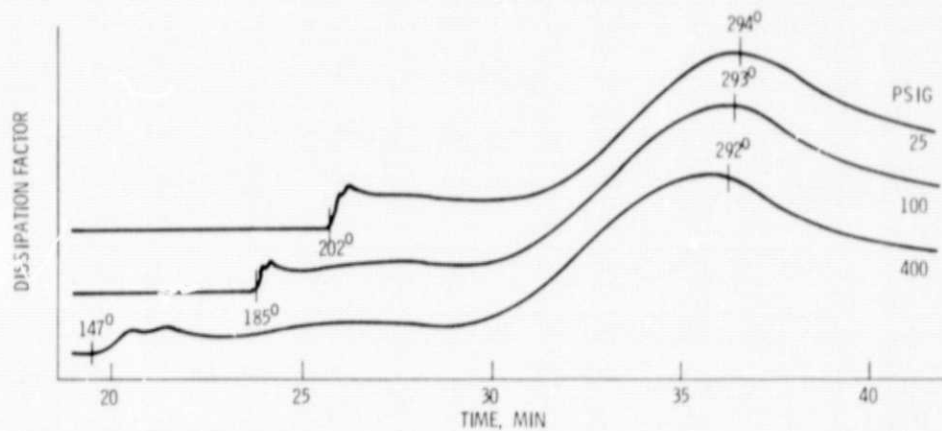


Figure 14. - Effect of pressure on change of DF with temperature and time for PMR 12.5 staged at 204° C for one hour (heat rate 9° C/min to 317° C; $f = 1$ kHz, 3 ply - 1 in.).

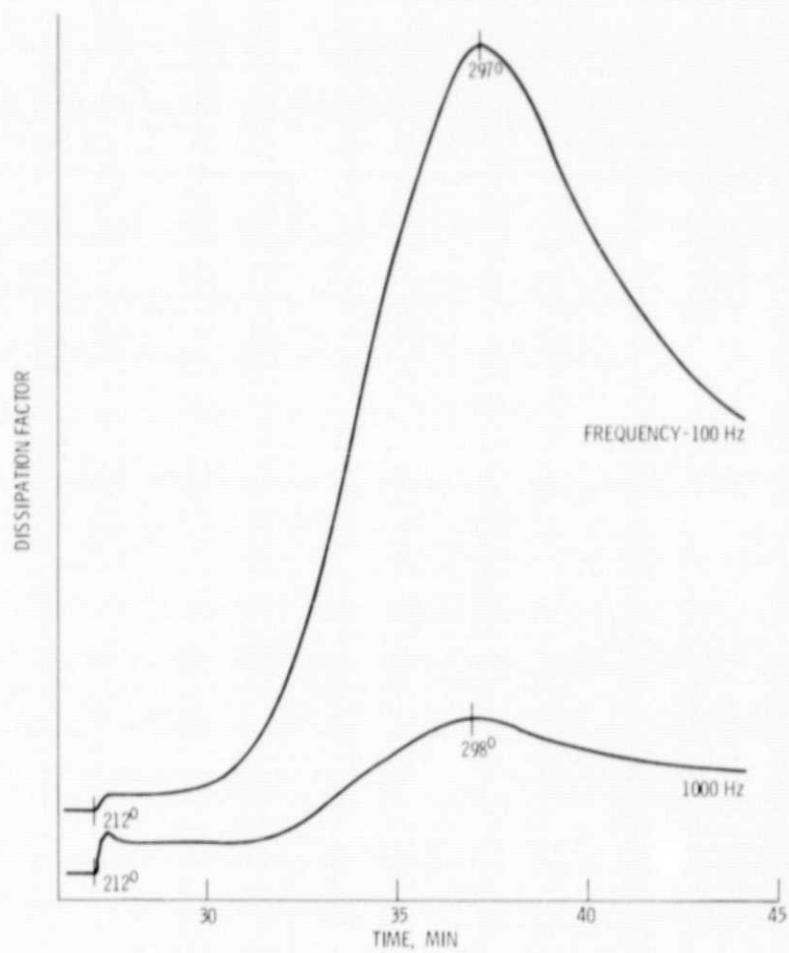


Figure 15. - Effect of frequency on DF change with temperature and time for PMR 15 staged at 204°C for one hour (heat rate 9°C/min to 317°C max, P = 25 psig, 3 ply - 1 in.²).

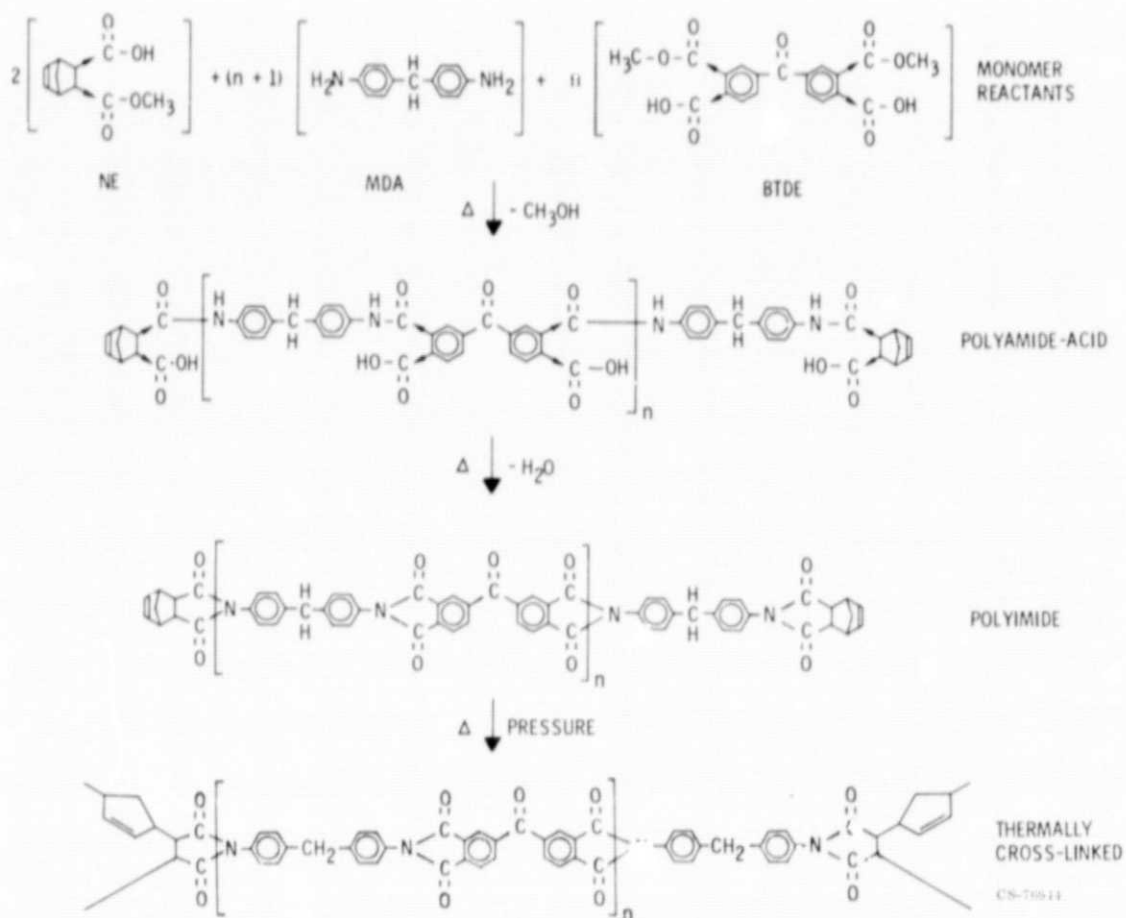


Figure 16. - PMR polyimide reaction sequence.